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(54) Alkaline storage battery and method of producing negative electrode thereof.

EP 0 386 305 A1 (57) Alkaline storage battery, in which the negative electrode is constituted by a hydrogen absorbing alloy capable of absorbing/desorbing hydrogen electrochemically, and a hydrophobic material and a hydrophilic material are provided in a portion of the surface layer of the negative electrode and in the side of the negative electrode respectively so as to properly secure both the wetting property and hydrophobic property of the negative electrode against the alkaline electrolytic solution. Accordingly, a hydrogen can be absorbed electrochemically in the portion of the negative electrode which is wetted by the electrolytic solution and a hydrogen gas generated in charging the battery can be absorbed by a vapor phase reaction in the hydrophobic portion of the negative electrode which is exposed to the vapor phase so that the internal gas pressure can be reduced to thereby make it possible to perform rapid charging.

follows. The method of adding a noble metal to the negative electrode has a problem in that the material cost is increased. On the other hand, the method of providing a hydrophobic layer in the negative electrode has a problem in that the discharging voltage is dropped because of the uneven electrolyte distribution of the negative electrode and the decrease of the effective surface area for the electrochemical reaction:

- 5 Further, the aforementioned method is effective for improvement in the oxygen absorption capacity of the negative electrode but has another problem in that the inner pressure of the battery is increased because hydrogen is apt to be generated from the negative electrode in charging the battery with lowering of the wetting property for the electrolytic solution, of the inside of the hydrogen absorbing alloy negative electrode. In particular, this fact is remarkable when the battery is charged rapidly.

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OBJECTS AND SUMMARY OF THE INVENTION

An object of the present invention is therefore to solve the aforementioned problems.

- 15 That is to say the object of the invention is to provide a hydrogen absorbing alloy negative electrode of a battery, in which wetting property of the inside of the negative electrode against an electrolytic solution can be improved while hydrophobic property of the surface of the negative electrode can be kept suitably, by which not only the internal gas pressure of the battery can be reduced in charging the battery rapidly but also voltage drop can be prevented in discharging the battery.

- 20 To solve the aforementioned problems, the present invention provides a construction of an alkaline storage battery in which a hydrophilic resin is provided to the inside of a negative electrode formed of a hydrogen absorbing alloy, and a hydrophobic resin is provided to the surface portion of the negative electrode, and also a method of producing the negative electrode of the above construction.

- In the construction and the producing method, according to the present invention, a hydrogen gas is absorbed into the hydrogen absorbing alloy by providing the hydrophobic resin to the surface of the hydrogen absorbing alloy negative electrode. Further, the wetting property of the inside of the hydrogen absorbing alloy negative electrode against an electrolytic solution is improved by use of the hydrophilic resin to make it easily to absorb hydrogen electrically, so that generation of a hydrogen gas can be prevented to thereby reduce the internal gas pressure of the battery in charging the battery rapidly. Further, the voltage drop in discharging the battery can be prevented by addition of the hydrophilic resin.

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DESCRIPTION OF THE DRAWINGS

- 35 Fig. 1 is a sectional view of a nickel-hydrogen storage battery produced according to the present invention;

Fig. 2 is a graph view showing the relation between charge electric capacity and internal gas pressure in the case where a charging current of 1 CmA at 20°C is respectively supplied to various hydrogen absorbing alloy negative electrodes different in construction;

- 40 Fig. 3 is a graph view showing the relation between the discharge electric capacity and the battery voltage in the case where a discharging current of 3 CmA at 20°C is respectively supplied to various hydrogen absorbing alloy negative electrodes different in construction;

- Fig. 4 is a graph view showing the relations among the quantity of FEP to be added, the internal gas pressure in the case where the battery is charged by 200% with respect to the positive electrode capacity with a charging current of 1 CmA at 20°C, and the intermediate voltage in the case where the battery is discharged to 0.18 V with a discharging current of 3 CmA at 20°C; and

- Fig. 5 is a graph view showing the relations among the quantity of PVA to be added, the internal gas pressure in the case where the battery is charged by 200% with respect to the positive electrode capacity with a charging current of 1 CmA at 20°C, and the intermediate voltage in the case where the battery is discharged to 0.8 V with a discharging current of 3 CmA at 20°C.

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DETAILED DESCRIPTION OF THE INVENTION

- The present invention will be described hereunder with respect to various examples. In the examples, the hydrogen absorbing alloy used for the negative electrode was $\text{MmNi}_{3.55}\text{Co}_{0.75}\text{Mn}_{0.4}\text{Al}_{0.3}$. Misch metal Mm (La: about 25 wt%, Ce: about 52 wt%, Nd: about 18 wt%, Pr: about 5 wt%) which was a mixture of rare-earth elements was put into an arc furnace together with other metal samples of Ni, Co, Mn and Al. The furnace was evacuated to obtain a vacuum state of from 10^{-4} to 10^{-5} Torr. Then the metal samples

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A hydrogen absorbing alloy negative electrode coated with polyethylene as a hydrophobic resin was prepared.

5 (Example 8)

A hydrogen absorbing alloy negative electrode coated with ethylene tetrafluoride (hereinafter referred to as "M-12") having a permeability coefficient of 1×10^{-9} cm/sec*atm for an oxygen/hydrogen gas was prepared.

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(Example 9)

A hydrogen absorbing alloy negative electrode coated with a hydrophobic resin by dipping the alloy powder into a solution of an FEP dispersion (hereinafter referred to as "ND-1") containing a surface active agent was prepared.

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(Example 10)

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A hydrogen absorbing alloy negative electrode coated with polyvinylidene fluoride (hereinafter referred to as "VDF") powder as a hydrophobic resin was prepared.

25 (Example 11)

A hydrogen absorbing alloy negative electrode coated with FEP by an amount of 0.1 mg/cm^2 was prepared.

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(Example 12)

A hydrogen absorbing alloy negative electrode coated with FEP by an amount of 2 mg/cm^2 was prepared.

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(Example 13)

A hydrogen absorbing alloy negative electrode coated with a 2 : 1 (weight proportion) mixture of platinum black capable of catalyzing the decomposition of hydrogen and FEP, by an amount of 2.4 mg/cm^2 , was prepared.

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(Example 14)

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A hydrogen absorbing alloy negative electrode coated with platinum black by an amount of 1.6 mg/cm^2 and then coated with FEP by an amount of 0.8 mg/cm^2 , was prepared.

50 (Example 15)

A hydrogen absorbing alloy negative electrode coated with a 4 : 1 (weight proportion) mixture of LaNi_4Al and FEP by an amount of 4.0 mg/cm^2 , was prepared.

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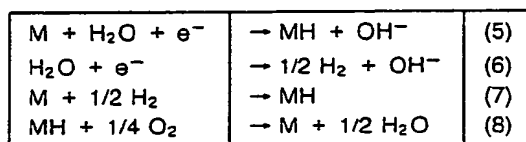
(Example 16)

A hydrogen absorbing alloy negative electrode coated with a 1 : 1 (weight proportion) mixture of

started when the battery had been charged to about 800 mAh. Through analyzing the gas composition generated in the battery upon completion of charging to 2000 mAh, the oxygen partial pressure was measured to be about 1 kg/cm² substantially equally in the all cases of the Examples 1 to 3. Accordingly, it was understood that the differences in the internal gas pressure of the battery among the three kinds of batteries were caused by differences in hydrogen partial pressure.

The reason is as follows.

In the nickel-hydrogen storage battery designed to have a high-capacity, for example, of 100 mAh in AA size, as shown in the present experiment, the balance of the negative electrode capacity (1600 mAh) against the positive electrode capacity (100 mAh) is not so sufficient that a reaction represented by the following equations (5) to (8) progresses on the hydrogen absorbing alloy negative electrode in charging the battery.



In the equations, M represents a hydrogen absorbing alloy. In short, the hydrogen absorbing reaction represented by the equation (5) and the hydrogen generation reaction represented by the equation (6) occur competitively in a portion of the negative electrode wetted by the electrolytic solution. Further, the reaction of consumption of an oxygen gas generated from the positive electrode, represented by the equation (8), occurs in the wetted portion at the same time. On the contrary, the hydrogen gas absorbing reaction (7), which hydrogen gas was generated according to the equation (6), progresses in another portion of the negative electrode which is not wetted by the electrolytic solution. The hydrophobic resin FEP acts to control the area of the hydrophobic portion on the hydrogen absorbing alloy negative electrode. It is apparent from the results of the Examples 2 and 3 that addition of the hydrophobic resin to the surface of the negative electrode is more effective than addition thereof to the inside of the negative electrode, and that the reaction of the equation (7) occurs mainly on the surface of the negative electrode. Comparing those examples, the Examples 2 and 3 are inferior in wetting property of the hydrogen absorbing alloy negative electrode for the electrolytic solution because of the addition of the hydrophobic resin. Accordingly, in the Examples 2 and 3, the effective surface area in the electrochemical reaction decreases, so that the charging current density increases to accelerate the hydrogen gas generation reaction of the equation (6) to make the rising of the internal gas pressure of the battery early and to increase the internal gas pressure rapidly. To solve this problem, PVA, which is a hydrophilic resin, was added to the inside of the electrode in the Example 1. As the result, the wetting property of the inside of the hydrogen absorbing alloy negative electrode particularly for the electrolytic solution was improved. As compared with the Examples 2 and 3, the Example 1 had an advantage in the point as follows. The charging current density was reduced by the increase of the effective surface area in the electrochemical reaction, so that the hydrogen gas generation reaction of the equation (6) was suppressed to delay the rising of the internal gas pressure of the battery to thereby reduce the internal gas pressure of the battery. For the aforementioned reason, in the Example 1 the increase of the internal gas pressure of the battery can be suppressed even in the case where the battery is charged rapidly with a charging current of 1 CmA.

Fig. 3 shows discharging curves in the cases where the three kinds of batteries of the respective Examples 1 to 3 were discharged with a discharging current of 3 CmA under the condition of 20° C. In Fig. 3, the battery voltage at an intermediate point of the discharge capacity when the battery has been discharged to 0.8 V is defined as an intermediate voltage for indicating the difference among the discharging voltages of the batteries.

Comparing the examples, the respective discharge capacities of the batteries are not different but the intermediate voltages are different remarkably. In the Example 1, the intermediate voltage was 1.150 V. In each of the Examples 2 and 3, the intermediate voltage was 1.100 V. In short, the difference between the intermediate voltages of the Example 1 and each of the Examples 2 and 3 was 50 mV.

The reason is as follows. In the Example 1, the wetting property of the inside of the negative electrode for the electrolytic solution was improved because hydrophilic resin PVA was added to the inside of the hydrogen absorbing alloy negative electrode. Accordingly, in the Example 1, the effective surface area in the electrochemical reaction increased to reduce the discharging current density as compared with the Examples 2 and 3, so that the discharge intermediate voltage increased.

negative electrode was examined as follows. In each of the Example 7 in which polyethylene was disposed on the surface of the negative electrode, the Example 8 in which M-12 having a permeability coefficient of 1×10^{-3} cm/sec atm for a hydrogen gas was disposed, the Example 9 in which ND-1 as a FEP dispersion containing a surface active agent in a solution was disposed, and the Example 10 in which VDF was disposed, the internal gas pressure of the battery in charging the battery was increased compared with the Example 1.

This is because the hydrophobic degree of the resin in each of the Examples 7 and 10 was smaller than that of FEP, so that a solid-gas interface for absorption of a hydrogen gas could not be formed sufficiently on the hydrogen absorbing alloy negative electrode.

In the Example 8, the solid-gas interface could be formed sufficiently on the hydrogen absorbing alloy negative electrode. However, the Example 8 was inferior in permeability of the negative electrode for a hydrogen gas generated by the electrochemical erection, so that in the Example 8 the internal gas pressure of the battery was increased. In the case where the hydrogen absorbing alloy negative electrode was coated with a hydrophobic resin having a small permeability coefficient for oxygen gas, the pressure of the battery in charging the battery was increased due to a inferiority of permeability of the negative electrode for an oxygen gas. In this case, from analyzing the gas composition, it was found that the proportion of oxygen increased compared with the Example 1. This is because the capacity of reducing an oxygen gas was reduced since the negative electrode was inferior in permeability for an oxygen gas.

In the Example 9, the solid-gas interface could not be formed sufficiently on the hydrogen absorbing alloy negative electrode in the same manner as in the Examples 7 and 10, because the surface active agent existing in the solvent of ND-1 was absorbed on FEP so that the negative electrode had a insufficient capacity of absorbing a hydrogen gas.

From the point of view of the structure of the battery safety vent or from the point of view of the strength of the battery case, it is preferable that the internal gas pressure of the battery in charging the battery is not higher than 5 kg/cm^2 . Accordingly, the conditions of preferred hydrophobic material to be disposed on the surface layer of the hydrogen absorbing alloy negative electrode is as follows.

(1) The material is selected from fluorine resins;

(2) The permeability coefficient for an oxygen gas or an hydrogen gas is not smaller than 1×10^{-3} cm/sec \cdot atm at 25°C ;

(3) When dispersion is used, no surface active agent is contained in the solvent; and

(4) The material is selected from the group consisting of poly(ethylene tetrafluoride) resin and ethylene tetrafluoridepropylene hexafluoride copolymer resin.

In the Examples 11 and 12, the quantity of the hydrophobic resin to be added to the surface layer of the hydrogen absorbing alloy negative electrode was examined as follows. In the Example 11, when the quantity of FEP to be added was 0.1 mg/cm^2 , the internal gas pressure of the battery in charging the battery was increased to 8.3 kg/cm^2 . In the Example 12, when the quantity of FEP to be added was 2 mg/cm^2 , the intermediate voltage in discharging the battery was reduced to 1.105 V because FEP acts as an insulating material to thereby increase the polarization of the hydrogen absorbing alloy negative electrode in discharging the battery. Fig. 4 shows the relations among the quantity of FEP to be added, the internal gas pressure of the battery in charging the battery and the intermediate voltage in discharging the battery. It is apparent from Fig. 4 that an optimum value exists in the quantity of FEP to be added. Accordingly, from the double viewpoint of the internal gas pressure of the battery in charging the battery and the intermediate voltage in discharging the battery, it is preferable that the hydrophobic resin is added to the surface layer of the hydrogen absorbing alloy negative electrode by an amount in the range of from 0.15 mg/cm^2 to 1.5 mg/cm^2 .

In the Examples 13 and 14, the effect by addition of a material capable of catalyzing the decomposition of a hydrogen gas, to the surface of the hydrogen absorbing alloy negative electrode and the method of addition thereof were examined. In the Example 13, the battery used a hydrogen absorbing alloy negative electrode coated with a mixture of platinum black capable of catalyzing the decomposition of a hydrogen gas and FEP acting as a hydrophobic material. In the Example 14, the battery used a hydrogen absorbing alloy negative electrode coated with platinum black and then coated with FEP. Referring to Table 1, in any case, the internal gas pressure of the battery in charging the battery was decreased and the intermediate voltage in discharging the battery was increased, compared with the battery of the Example 1 using the hydrogen alloy negative electrode coated with FEP. This is because, by the addition of platinum black, the hydrogen gas absorbing reaction on the hydrogen absorbing alloy electrode as represented by the equation (7) was accelerated in charging the battery and the hydrogen desorbing reaction on the hydrogen absorbing alloy was accelerated in discharging the battery. Although the examples have shown the case where platinum black was used as a material capable of catalyzing the decomposition of a hydrogen gas, it is a

absorbing alloy is increased, the charging/discharging characteristics are improved. However, the increase of the porosity is not preferable from the point of view of high energy density of the hydrogen absorbing alloy negative electrode and battery. Accordingly, the preferred porosity of the hydrogen absorbing alloy negative electrode is in the range of from 20 to 40 vol%.

5 The method of addition of the hydrophobic material to the surface of the hydrogen absorbing alloy negative electrode was examined as follows. The Example 1 relates to a battery using a negative electrode formed by the steps of: mixing hydrogen absorbing alloy powder and an aqueous solution of PVA to prepare paste; filling a foamed nickel matrix as a three-dimensional supporting matrix with the paste; pressing the supporting matrix containing the paste; and applying FEP to the surface of the negative
10 electrode. The Example 19 relates to a battery using a negative electrode formed by pressing the supporting matrix after applying FEP to the surface of the supporting matrix containing the paste. It was apparent from Table 1 that the internal gas pressure of the battery in charging the battery in the Example 19 was increased to 11.2 kg/cm² compared with the Example 1. This is because FEP in the Example 19 was distributed into the inside of the hydrogen absorbing alloy negative electrode by pressing the
15 supporting matrix, so that the hydrophilic property of the inside of the hydrogen absorbing alloy negative electrode was deteriorated and the electrochemical hydrogen absorbing reaction of the equation (5) was suppressed to thereby accelerate generation of a hydrogen gas in charging the battery. For the reason, the preferred method of producing a hydrogen absorbing alloy negative electrode is the method of the Example 1 comprising the steps of: mixing hydrogen absorbing alloy powder and an aqueous solution of PVA to
20 prepare paste; applying the paste to a supporting matrix through selected one of filling, injecting and smearing; pressing the supporting matrix and applying FEP to the surface thereof by selected one of smearing, dipping and injecting. This hydrogen absorbing alloy negative electrode production method can be applied to the case where the surface of the hydrogen absorbing alloy negative electrode contains a material capable of catalyzing the decomposition of a hydrogen gas, an electric conductive material and
25 hydrogen absorbing alloy powder having a hydrogen equilibrium pressure lower than that of $\text{MmNi}_{3.55}\text{Mn}_{0.4}\text{Al}_{0.3}\text{Co}_{0.75}$. In this case, it is preferable that the aforementioned materials and mixtures of the materials and FEP are applied to the surface of the hydrogen absorbing alloy negative electrode through selected one of smearing, dipping and injecting after pressing the supporting matrix containing the paste consisting of hydrogen absorbing alloy powder and an aqueous solution of PVA.

30 The Example 20 relates to a battery using a negative electrode prepared by the steps of: filling a supporting matrix with paste consisting of hydrogen absorbing alloy powder and an aqueous solution of PVA; pressing the supporting matrix to prepare a hydrogen absorbing alloy negative electrode, and adding FEP to the surface of the negative electrode through dipping the negative electrode into a PVA aqueous solution containing FEP. The charging/discharging characteristics of the battery of the Example 20 were as
35 follows. The internal gas pressure of the battery in charging the battery was 3.5 kg/cm² and the intermediate voltage in discharging the battery was 1.175 V. It is apparent from comparison with the Example 1 that the discharging characteristic of the battery of the Example 20 has been improved. Further, the internal gas pressure of the battery using the negative electrode of the Example 20 was not deteriorated even in the case where charge/discharge was repeated over 500 cycles. This is because FEP is fixed firmly to the
40 surface of the negative electrode by polyvinyl alcohol. As described above, another preferred method of producing a hydrogen absorbing alloy negative electrode according to the invention may comprises the steps of: mixing hydrogen absorbing alloy powder and an aqueous solution of PVA to prepare paste; applying the paste to a supporting matrix through selected one of filling, dipping and injecting; pressing the supporting matrix; and applying a mixture of a hydrophilic material and a hydrophobic material to the
45 surface of the negative electrode through selected one of smearing, dipping and injecting.

It is to be understood that polyvinyl alcohol may be replaced by one of other alkali-resisting resins such as carboxymethylcellulose and methylcellulose and the same effect can be obtained by the other alkali-resisting resins.

A further battery was prepared as follows. A mixture of FEP and polyethylene at a weight ratio of 2 : 1
50 was applied to the surface of the hydrogen absorbing alloy negative electrode by an amount of FEP of 0.8 mg/cm². Then the negative electrode was heated at 120° C for 30 minutes. The battery was prepared by using the thus prepared negative electrode. The internal gas pressure of the battery in charging the battery was 3.5 kg/cm² and the intermediate voltage thereof in discharging the battery was 1.150 V. Those obtained values were substantially the same as those in the Example 1. However, the internal gas pressure of the
55 battery was not deteriorated in the same manner as in the Example 20 even in the case where charge/discharge was repeated over 500 cycles. This is because FEP was fixed firmly to the surface of the negative electrode by polyethylene. Polyethylene used herein may be replaced by one of thermoplastic resins, such as polypropylene, polyvinyl chloride, ABS resin and polystyrene, having a melting point lower

hydrogen absorbing alloy negative electrode is represented by the general composition formula $A_{1-x}B_xC_y$, in which A is selected from the group consisting of La, mixtures of La and rare-earth elements, and misch metal; B is selected from the group consisting of Ti, Zr, Ca, Y, Hf and mixtures thereof; x has a value within the range $0 \leq x \leq 0.2$; C is selected from the group consisting of Ni, Co, Mn, Al, Fe, Cu, Cr and mixtures thereof; and y has a value within the range $4.7 \leq y \leq 5.3$, made up as follows, $y > 3.5$ for Ni, $y \leq 1.0$ for Co, $y \leq 0.6$ for Mn, $y \leq 0.5$ for Al, $y \leq 0.3$ for Fe, $y \leq 1.0$ for Cu, and $y \leq 0.3$ for Cr.

Further, V was added to the aforementioned hydrogen absorbing alloy to prepare a hydrogen absorbing alloy represented by the formula $MmNi_{3.55}Co_{0.75}Mn_{0.4}Al_{0.3}V_{0.02}$. When the negative electrode of the battery was formed of the alloy, the internal gas pressure of the battery in charging the battery was 2.8 kg/cm² and the intermediate voltage in discharging the battery was 1.158 V. Thus, the battery was improved compared with the Example 1. This is because the lattice constant of the hydrogen absorbing alloy was increased by addition of V thereby hydrogen can diffuse rapidly in the hydrogen absorbing alloy phase. The effect by addition of V was found when V was added by an amount of larger than 0.02 atomic ratio. However, when V was added by an amount of not smaller than 0.3, the alloy phase effective for absorbing hydrogen was reduced so that the discharge capacity was undesirably reduced. Accordingly, it is preferable to add V by an amount in the range of from 0.02 to 0.3 atomic ratio.

Further, In was added to the aforementioned hydrogen absorbing alloy to prepare a hydrogen absorbing alloy represented by the formula $MmNi_{3.55}Co_{0.75}Mn_{0.4}Al_{0.3}In_{0.02}$. When a battery was prepared by using the alloy in the negative electrode thereof, the internal gas pressure of the battery in charging the battery was 2.5 kg/cm². In short, the charging characteristic of the battery was improved compared with the Example 1. This is because the hydrogen over voltage of the hydrogen absorbing alloy negative electrode in charging the battery was increased to suppress generation of hydrogen. The effect by addition of In was found when In was added by an amount of larger than 0.02 atomic ratio. However, when In was added by an amount of not smaller than 0.1, the discharge capacity was undesirably reduced. Accordingly, it is preferable to add In by an amount in the range of from 0.02 to 0.1 atomic ratio. The same effect was obtained in the case where In was replaced by Ti or Ga.

Having described the case where the invention is applied to a nickel-hydrogen storage battery, it is a matter of course that the invention is applicable to other alkaline storage batteries, such as a manganese dioxide-hydrogen storage battery, using a hydrogen absorbing alloy negative electrode.

As described above, according to the present invention, a hydrogen absorbing alloy negative electrode containing a hydrophilic resin in the inside thereof and a hydrophobic resin or hydrophobic material in the surface thereof, which hydrophobic material has powder of a hydrogen absorbing alloy having a hydrogen equilibrium pressure lower than that of the main hydrogen occlusion alloy, an electric conductive material and a material capable of catalyzing the decomposition of hydrogen gas, is provided by the steps of: mixing hydrogen absorbing alloy powder and a hydrophilic material to prepare paste; applying the paste to a supporting matrix through selected one of filling, injecting and smearing; pressing the supporting matrix; and applying a material containing a hydrophobic resin to the surface of the negative electrode by selected one of smearing, dipping and injecting. Accordingly, an effect arises in that a sealed alkaline storage battery free from the increase of the internal gas pressure in overcharging of the battery and free from the decrease of the battery voltage in discharging the battery can be provided.

Claims

1. An alkaline storage battery comprising: a positive electrode containing a metal oxide as a main constituent material thereof; a negative electrode containing, as a main constituent material thereof, a hydrogen absorbing alloy capable of electrochemically absorbing/desorbing hydrogen acting as an active material; an alkaline electrolytic solution; a separator; and said negative electrode including a hydrophobic material disposed in at least a part of an electrode surface layer thereof and including a hydrophilic material disposed in the inside thereof.

2. An alkaline storage battery according to Claim 1, in which said hydrogen absorbing alloy of said negative electrode is represented by the general composition formula $A_{1-x}B_xC_y$, in which A is selected from the group consisting of La, mixtures of La and rare-earth elements, and misch metal; B is selected from the group consisting of Ti, Zr, Ca, Y, Hf and mixtures thereof; x has a value within the range $0 \leq x \leq 0.2$; C is selected from the group consisting of Ni, Co, Mn, Al, Fe, Cu, Cr and mixtures thereof; and y has a value within the range $4.7 \leq y \leq 5.3$, made up as follows, $y > 3.5$ for Ni, $y \leq 1.0$ for Co, $y \leq 0.6$ for Mn, $y \leq 0.5$ for Al, $y \leq 0.3$ for Fe, $y \leq 1.0$ for Cu; and $y \leq 0.3$ for Cr.

3. An alkaline storage battery according to Claim 1, in which said hydrogen absorbing alloy of said

mixing hydrogen absorbing alloy particles and an aqueous solution of hydrophilic resin to prepare paste; applying said paste to a supporting material through selected one of filling, injecting and smearing; pressing said supporting material containing said paste; and applying a hydrophobic material to the surface of the thus prepared electrode through selected one of smearing, dipping and injecting.

5 21. A method of producing an alkaline storage battery negative electrode according to Claim 20, further comprising the step of coating the surface of the hydrogen absorbing alloy negative electrode with a mixture of a hydrophobic material and a material capable of catalyzing the decomposition of hydrogen gas, through selected one of smearing, dipping and injecting.

10 22. A method of producing an alkaline storage battery negative electrode according to Claim 20, further comprising the steps of coating the surface of the hydrogen absorbing alloy negative electrode with a material capable of catalyzing the decomposition of a hydrogen gas through selected one of smearing, dipping and injecting, and further coating the surface of the coating of the material capable of catalyzing the decomposition of a hydrogen gas with a hydrophobic material through selected one of smearing, dipping and injecting.

15 23. A method of producing an alkaline storage battery negative electrode according to Claim 20, further comprising the step of applying a mixture of a hydrophobic material and an electric conductive material to the surface of the hydrogen absorbing alloy negative electrode through selected one of smearing, dipping and injecting.

20 24. A method of producing an alkaline storage battery negative electrode according to Claim 20, further comprising the step of applying a mixture of a hydrophobic material and particles of another hydrogen absorbing alloy having a hydrogen equilibrium pressure lower than that of said hydrogen absorbing alloy, to the surface of the hydrogen absorbing alloy negative electrode surface, through selected one of smearing, dipping and injecting.

25 25. A method of producing an alkaline storage battery negative electrode according to Claim 20, further comprising the step of applying a mixture of a hydrophobic material and a binding agent to the surface of the hydrogen absorbing alloy negative electrode through selected one of smearing, dipping and injecting.

30 26. A method of producing an alkaline storage battery negative electrode according to Claim 20, further comprising the steps of: applying a mixture of a hydrophobic material and a thermoplastic resin to the surface of the hydrogen absorbing alloy negative electrode through selected one of smearing, dipping and injecting; and heating the surface coated with said mixture at a temperature at which said thermoplastic resin is melted but said hydrophobic material is not melted.

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FIG. 2

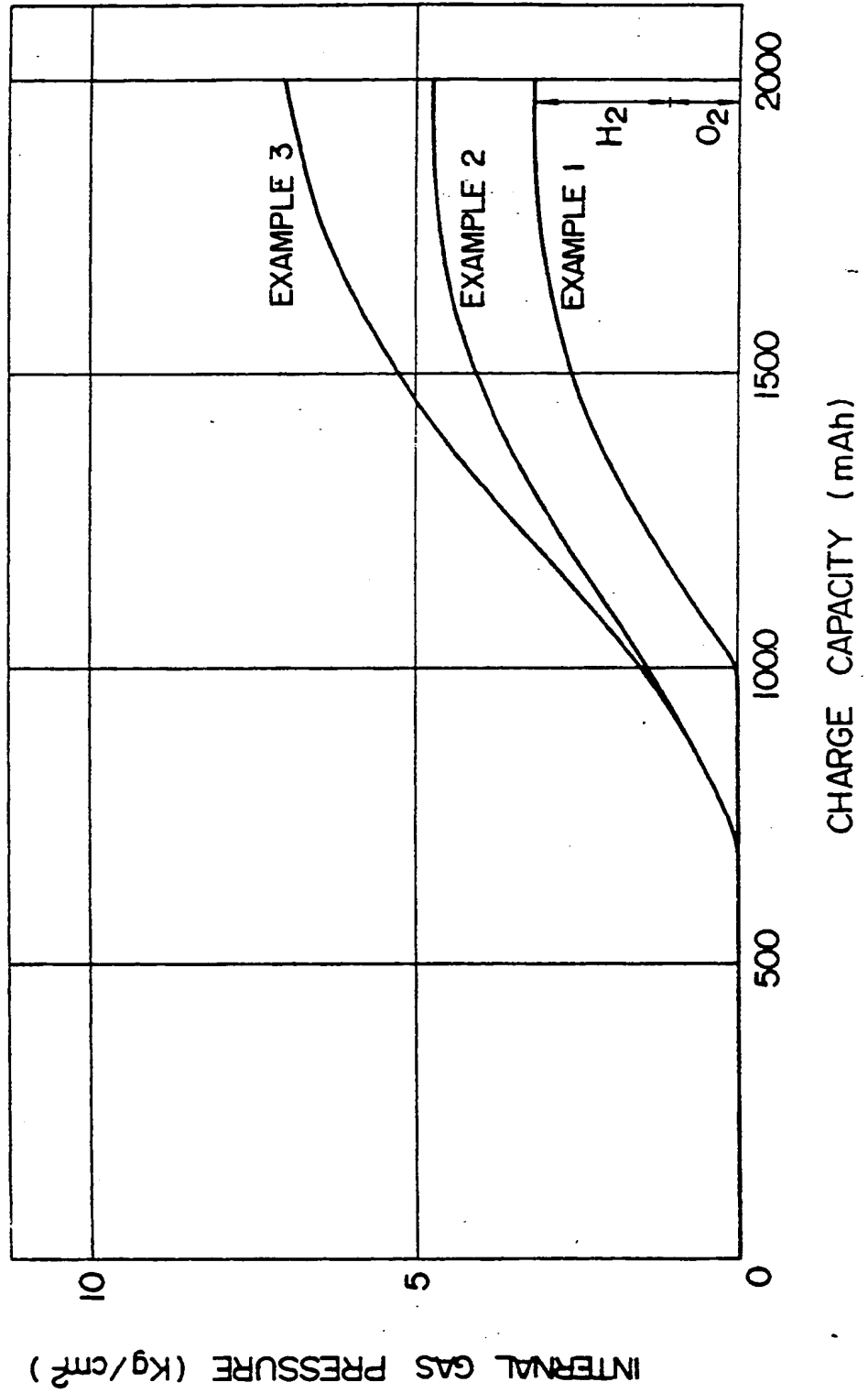
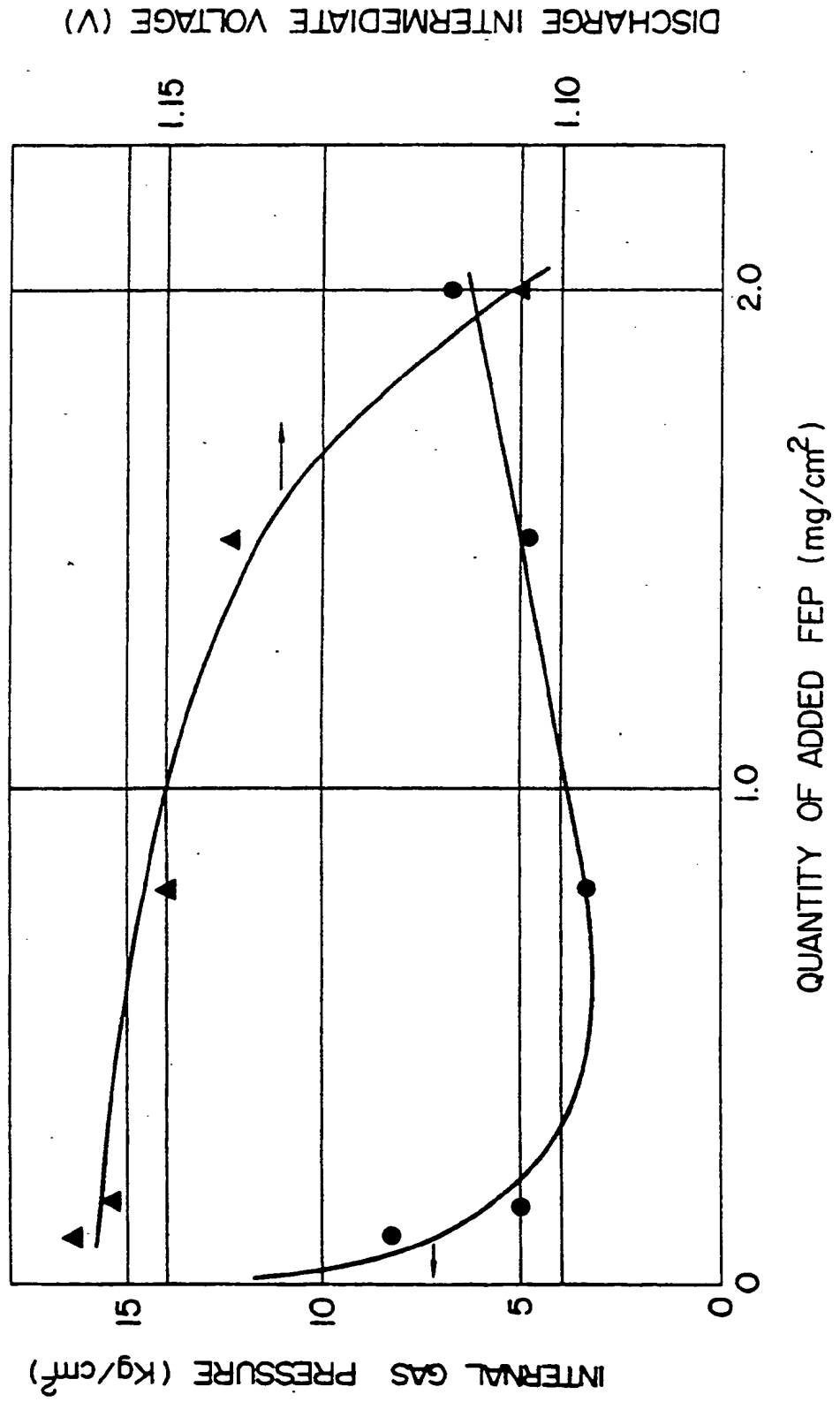


FIG. 4





European Patent
Office

EUROPEAN SEARCH REPORT

Application Number

EP 89-10 9749

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.5)
X	CHEMICAL ABSTRACTS, vol. 107, no. 18, 2nd November 1987, page 249, abstract no. 158314t, Columbus, Ohio, US; & JP-A-62 139 255 (MATSUSHITA ELECTRIC INDUSTRIAL CO., LTD) 22-06-1987 * Abstract *	1,2,5,6 9,15, 20	H 01 M 4/00 H 01 M 4/38 H 01 M 10/34
Y	IDEM	3,4,11, 13,16, 19,22, 23	
Y	FR-A-2 382 774 (ANVAR) - * Claims 1-8,10,13; page 2, lines 22-36; page 3, lines 4-34; page 6, lines 17-20; page 7, lines 4-6; example 4 *	3	
Y	JP-A-63 304 570 (MATSUSHITA ELECTRIC IND.) * Tabel (example N), page 404 * & PATENT ABSTRACTS OF JAPAN, vol. 13, no. 142 (E-739)[3490], 7th April 1989	3	
Y	CHEMICAL ABSTRACTS, vol. 109, no. 26, 26th December 1988, page 193, abstract no. 234219z, Columbus, Ohio, US; & JP-A-63 195 960 (MATSUSHITA ELECTRIC INDUSTRIAL CO., LTD) 15-08-1988 * Abstract *	13,23	
Y	CHEMICAL ABSTRACTS, vol. 104, no. 18, 5th May 1986, page 209, abstract no. 152446d, Columbus, Ohio, US; & JP-A-60 220 556 (MATSUSHITA ELECTRIC IND. CO., LTD) 05-11-1985 * Abstract *	16,19	
The present search report has been drawn up for all claims			
Place of search		Date of completion of the search	Examiner
THE HAGUE		08-06-1990	D'HONDT J.W.
CATEGORY OF CITED DOCUMENTS			
X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document			
T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document			

EP FORM 1503 (01.82) (P0401)



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EUROPEAN SEARCH REPORT

Page 3

Application Number

EP 89 10 9749

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.5)
A	PATENT ABSTRACTS OF JAPAN, vol. 10, no. 61 (E-387)[2118], 11th March 1986; & JP-A-60 212 958 (MATSUSHITA DENKI SANGYO K.K.) 25-10-1985 * Abstract *	12	
A	CHEMICAL ABSTRACTS, vol. 100, no. 18, 30th April 1984, page 182, abstract no. 142237q, Columbus, Ohio, US; & JP-A-58 46 830 (MATSUSHITA ELECTRIC INDUSTRIAL CO., LTD) 19-10-1983 * Abstract *	1,9	
			TECHNICAL FIELDS SEARCHED (Int. Cl.5)
The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 08-06-1990	Examiner D'HONDT J.W.
<div>CATEGORY OF CITED DOCUMENTS</div> <div>X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document</div> <div>T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document</div>			

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